



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

X-ray Emission Spectroscopy in Magnetic 3d-Transition Metals

Valentin Iota, Jae-Hyun Park, Bruce Baer,
Choong-Shik Yoo, Guoyin Shen

November 19, 2003

Advanced Photon Source Annual Progress Report

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

Authors: Valentin Iota: iota1@llnl.gov
Jae-Hyun Park: Park10@llnl.gov
Bruce Baer: Baer4@llnl.gov
Choong-Shik Yoo: yoo1@llnl.gov
Guoyin Shen: shen@cars.uchicago.edu

ReportID: iota3b0420bca5

Beamline: 13ID-D(GSE -CARS)

Scientific Discipline: Materials Science/Condensed -Matter Physics

X-ray Emission Spectroscopy in Magnetic 3d-Transition Metals

V. Iota¹, J.-H. Park¹, B. Baer¹, C.S. Yoo¹, G. Shen²

¹*Lawrence Livermore National Laboratory
University of California, Livermore CA 94550*

²*Consortium for Advanced Radiation Sources,
University of Chicago, Chicago IL*

Introduction:

The application of high pressure affects the band structure and magnetic interactions in solids by modifying nearest neighbor distances and interatomic potentials. While all materials experience electronic changes with increasing pressure, spin polarized, strongly electron correlated materials are expected to undergo the most dramatic transformations. In such materials, (*d* and *f*-electron metals and compounds), applied pressure reduces the strength of on-site correlations, leading to increased electron delocalization and, eventually, to loss of its magnetism. In this ongoing project, we study the electronic and magnetic properties of Group VIII, 3d (Fe, Co and Ni) magnetic transition metals and their compounds at high pressures.

The high-pressure properties of magnetic 3d-transition metals and compounds have been studied extensively over the years, because of iron being a major constituent of the Earth's core and its relevance to the planetary modeling to understand the chemical composition, internal structure, and geomagnetism. However, the fundamental scientific interest in the high-pressure properties of magnetic 3d-electron systems extends well beyond the geophysical applications to include the electron correlation-driven physics. The role of magnetic interactions in the stabilization of the "non-standard" ambient pressure structures of Fe, Co and Ni is still incompletely understood. Theoretical studies have predicted (and high pressure experiments are beginning to show) strong correlations between the electronic structure and phase stability in these materials. The phase diagrams of magnetic 3d systems reflect a delicate balance between spin interactions and structural configuration. At ambient conditions, the crystal structures of α -Fe (*bcc*) and ϵ -Co (*hcp*) phases depart from the standard sequence (*hcp* \rightarrow *bcc* \rightarrow *hcp* \rightarrow *fcc*), as observed in all other non-magnetic transition metals with increasing the *d*-band occupancy, and are different from those of their 4*d*- and 5*d*-counterparts. This anomalous behavior has been interpreted in terms of the spin-polarized *d*-band altering the *d*-band occupancy [1]. At high pressures, however, the *d*-valence band is expected to broaden resulting in a suppression or even a complete loss of magnetism. Experimentally, ferromagnetic α (*bcc*)-Fe has been confirmed to transform to non-magnetic ϵ -Fe (*hcp*) at 10 GPa [2,3]. Recently, we have also observed a similar transition in Co from ferromagnetic α (*hcp*)-Co to likely nonmagnetic β (*fcc*)-Co at 105 GPa [4]. A similar structural phase transition is expected in Ni, probably in the second-order *fcc* \rightarrow *fcc* transition. However, there has been no directly measured change in magnetism associated with the structural phase transition in Co, nor has yet been confirmed such an iso-structural phase transition in Ni.

Similar electronic transitions have been proposed in these 3d-transition metal oxides (FeO, CoO and NiO) from high spin (magnetic) to low spin (nonmagnetic) states [5]. In each of these systems, the

magnetic transition is accompanied by a first-order structural transition involving large volume collapse (10% in FeO, for example). So far, there have been no electronic measurements under pressure confirming these significant theoretical predictions, although the predicted pressures for the volume collapse transitions are within the experimental pressure range (80–200 GPa).

Methods and Materials:

In our experiments, we use synchrotron based *X-ray emission spectroscopy* (XES) of the $K\beta$ transition to determine the spin state of 3d transition metals and transition metal oxides under pressure. In $K\beta$ XES, 1s core electrons are excited by high-energy polychromatic x-rays from a highly collimated synchrotron source (13ID-D, GSECARS). The resulting $K\beta$ emission is analyzed using a high-resolution (1 eV) analyzer/detector system to determine the polarization of the valence band electrons. For the 3d transition elements, the $K\beta$ line ($3p \rightarrow 1s$ transition) contains information about the polarization of the valence band via the $3p-3d$ exchange interaction. The separation, ΔE , and intensity ratio, I'/I , of the multiplet transition, can be used to determine the number of unpaired electrons in d-states, $2S$, and the exchange integral, J , as $\Delta E = J(2S+1)$, and $I'/I = 2S/(2S+2)$ [6].

Traditionally, the limiting factor in the DAC-XES experiments in 3d elements is that the $K\beta$ emission photons (7–8 keV) are strongly attenuated by the diamond anvils. In addition, the small band splitting requires the use of high-intensity x-rays from collimated 3rd generation synchrotron sources, unavailable until recently for use in the DAC. To avoid the absorption of XES signal by the diamond anvils, our XES measurements have been conducted in a radial configuration, using hardened Be gaskets [7]. This allows simultaneous access along the axial direction, for use for in-situ laser-heating, on-line ruby pressure measurements, or x-ray diffraction measurements.

Results:

We have performed XES measurements of the $K\beta$ emission in Fe up to pressures of 50 GPa. In the low pressure phase (ferromagnetic), in addition to the main, narrow $K\beta_{1-3}$ peak, we observe a low energy satellite ($K\beta'$)—associated with transitions into the downspin state of the 3p orbital (i.e. in the final state of the transition the total spin of the 3p core-hole is aligned opposite to the magnetic moment of the valence band).

At pressures between 12–25 GPa, we observe the gradual disappearance of the $K\beta'$ satellite, indicating an electronic transition to a low-spin state. Our data shows that the quenching of the magnetism in Fe occurs concurrently with the structural transformation to the high pressure (hcp) structure (as determined from diffraction experiments). This result agrees with the report by Rueff et al. [3].

In our first experiment, we observed a small but measurable positive shift in energy of the main $K\beta$ peak with applied pressure (~ 1 eV/GPa). However, our subsequent careful measurements, using remotely controlled membrane-type DACs to avoid sample motion in the beam, did not corroborate the original results. Comparison of the two experiments suggests that the error in the original result was caused by minor—but systematic—changes in beam position on the sample during pressure increase. Our analysis also shows that beam position changes do not affect the intensity of the $K\beta'$ satellite band, and therefore, do not affect the conclusions relating to the spin state of the valence band.

Figure 1 shows the results of four XES measurements under pressure on magnetite (Fe_3O_4) using membrane DACs with Be gaskets. Our results show that, between 42 GPa and 48 GPa, the intensity of the $K\beta'$ satellite (a measure of valence band spin polarization) decreases, stabilizing at a non-zero value. We interpret this to

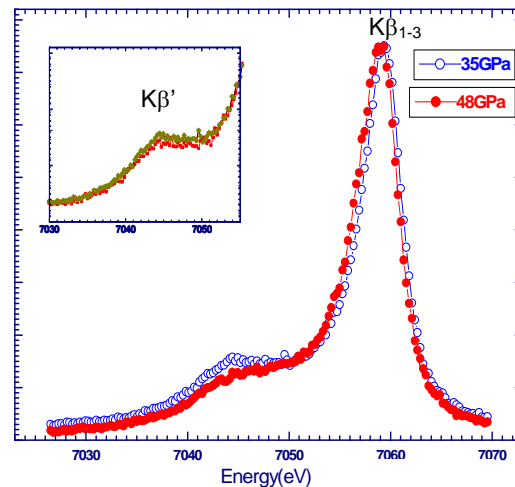


Fig.1: XES measurements of the $K\beta$ emission in magnetite (Fe_3O_4) at high pressure. Starting around 38 GPa, the intensity of the $K\beta$ band decreases, indicating an electronic transition.

indicate an electronic transition to an “intermediate spin” state. Further increases in pressure did not reduce the residual intensity of the $K \beta'$ emission up to 60 GPa.

This result stands in contrast with the published XES data of hematite (Fe_2O_3) under pressure (and with our own measurements of Fe_2O_3): in hematite, a strong suppression of the $K \beta'$ line in magnetite suggests that the final electronic state is a “low spin” state, with paired electron spins in the valence band [8].

Discussion:

Our analysis of the observed changes in $K \beta$ line shape in Fe_3O_4 under pressure suggests the dissociation of magnetite into FeO and Fe_2O_3 . The resulting high-pressure phase of hematite is in a low spin state, while the FeO maintains the polarization of the valence band at least to 143 GPa [9]. The result is an “intermediate spin” state of the dissociated magnetite, with the observed reduced intensity $K \beta'$ emission originating from the divalent iron sites. Above 50 GPa, the contribution of the low spin state of Fe^{3+} to the total spin is negligible.

Acknowledgments:

This work was performed at GeoSoilEnviroCARS (Sector 13), Advanced Photon Source (APS), Argonne National Laboratory. GeoSoilEnviroCARS is supported by the National Science Foundation Earth Sciences (EAR-0217473), Department of Energy - Geosciences (DE-FG02-94ER14466) and the State of Illinois. Use of the APS was supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Energy Research, under Contract No. W-31-109-Eng-38. Work at Lawrence Livermore National Laboratory was supported by the LDRD and PDRP programs at the LLNL, University of California under the auspices of the U.S. -DOE under contract number W-7405-ENG-48.

References:

1. P. Soderlind et al., Phys. Rev. B **50**, 5918 (1994); Phys. Rev. B **53**, 14063 (1996).
2. H. K. Mao, et al. J. Appl. Phys. **38**, 272 (1967)
3. J. P. Rueff, M. Krisch, Y. Q. Cai, A. Kaprolat, M. Hanfland, M. Lorenzen, C. Masciovecchio, R. Verbeni, and F. Sette, Phys. Rev. B **60**, 14510-14512 (1999)
4. C.-S. Yoo et al., Phys. Rev. Lett., **84**, 4132-4135 (2000)
5. M. Cohen et al., Science **275**, 657 (1997)
6. X. Wang, F. M. F. de Groot, and S. P. Cramer, Phys. Rev. B **56**, 4553 (1997).
7. R. J. Hemley, H. K. Mao, G. Shen, J. Badro, P. Gillet, M. Han and, D. Häusermann, Science **276**, 1242 (1997).
8. J. Badro, G. Fiquet, V. V. Struzhkin, M. S. Somayazulu, H. K. Mao, G. Shen, and T. Le Bihan. Phys. Rev. Lett. **89**, 205504 (2002).
9. J. Badro, V. V. Struzhkin, J. Shu, R. J. Hemley, H. K. Mao, C.-C. Kao, J.-P. Rueff, and G. Shen. Phys. Rev. Lett. **83**, 4101 (1999).